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Jahn–Teller effect in $^4T_{2g}$ excited state of Mn^{2+}:MgO

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ABSTRACT

The aim of this paper is the estimations the electron-vibrational interaction constants, Huang–Rhys factors and Jahn–Teller stabilization energy, in $^4T_{2g}$ excited state of divalent manganese, doped in magnesium oxide single crystal, using two methods of calculations.

First method is based on the exchange charge model of crystal field and has been applied to determine the dependence of crystal field strength $10Dq$ on R distance between divalent manganese impurity ion and oxygen ligands, in octahedral site symmetry. Obtained results were extrapolated by the power law and was shown that $10Dq$ depends on R as $1/R^n$, with $n = 5.785$. This deviations from value $n = 5$, predicted by the simple point charge model of crystal field, is explained by the covalent and exchange effects. The second method is based on Ham quenching of the spin–orbit splitting of $^4T_{2g}$ excited state, described by the effective second-order spin-Hamiltonian.

The obtained values for electron-vibrational interaction constants, Huang–Rhys parameters and Jahn–Teller stabilization energy were compared between them and discussed. Comparison of the results with experimental data are quite satisfactory and confirm the reliability of exchange charge model and Ham reduction scheme for the title system.

1. Introduction

Magnesium oxide (MgO) single crystal is usually regarded as a model system to investigate magnetic [1,2], absorption [3,4], structural [5,6] and optical properties [7] of doped transition-metal $3d^n$ ions, as impurity ions. Also, it is a good candidate for tunable laser operation [8] and for the study of the Jahn–Teller effect (JTE) [9]. The mechanism responsible for all the manifestations of the JTE is the coupling between the vibrations of the surrounding ions and the localized electronic wavefunctions of the impurity ion. This type of interactions is usually named as electron-vibrational interactions (EVI), or vibronic coupling [9]. These interactions are characterized by typical parameters as EVI coupling constants, Huang–Rhys (HR) factors and Jahn–Teller stabilization energy (E_{JT}). It is also worthwhile to note that it is possible to establish a close relation between the crystal field effects, covalent effects (overlap between the wave functions of the impurity ion and ligands) and JTE. The existence of a dynamic JTE in the $^4T_{2g}$ multiplet of MgO:Mn^{2+} is evidenced, also, by quenching of the spin–orbit interaction (Ham effect) – characterized by the Ham reduction parameter, as measure of the strength of the dynamic JTE. Therefore, the doped MgO:Mn^{2+} represents a prototypical system for study and testing theoretical models of crystal field theory and JTE, being an interesting problem to pursue.

The divalent manganese ion (Mn^{2+}) ion doped in MgO crystal, as impurity ion, will substitute divalent magnesium ion (Mg^{2+}) and will be coordinated by a perfect octahedron of oxygen ions (O^{2-}).

It is well-known [10] that the energy levels of an impurity $3d^n$ ion in a crystal are split by crystal field (CF), and the character of this splitting depends on many factors: electrical charges of ions, interionic separation, etc. In cubic crystal fields, in absence of spin–orbit interaction, this splitting is characterized by crystal field strength $10Dq$ and B, C Racah parameters [10].

The simplest point charge model (PCM) of CF describes dependence of $10Dq$ on interionic distance as $\sim 1/R^5$ [11]. A number of works [12–19] employing quantum–mechanical calculations reported the values of n in a rather wide interval from 3.5 to 7.3 , for different systems. This deviations from $n = 5$ value, predicted by the simple PCM of CF, can be explained by the covalent and exchange effects.

So, in the first approximation of a cluster model, $10Dq$ depends on Mn^{2+}–O^{2-} distance which can be divided in two contributions, one $10Dq$(PC), coming from the point charges (PC) and second one $10Dq$(EC), due to covalent interactions (EC) of the impurity ion with ligands

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$$10Dq = 10Dq(\mathrm{PC}) + 10Dq(\mathrm{EC}) \tag{1}$$

First term in Eq. (1) was calculated in the frame of PCM of CF theory and for the second contribution, we considered the d orbitals of cation mixing with *p* and *s* valence orbitals of the ligands, in the frame of exchange charge model (ECM) [20] of CF. They are given by [20]

$$10Dq(\mathrm{PC}) = -\frac{5}{672}e^2\langle r^4\rangle\sum_i q_i\frac{V_4^0(\theta(i),\varphi(i))}{R(i)^5} \tag{2}$$

$$10Dq(\mathrm{EC}) = \frac{3}{112}e^2\sum_i\left[S(s)_i^2 + S(\sigma)_i^2 - \frac{4}{3}S(\pi)_i^2\right]\frac{V_4^0(\theta(i),\varphi(i))}{R(i)}G \tag{3}$$

The sums are carried out over lattice ions denoted by i with charges q_i; $R(i)$, $\theta(i)$, $\varphi(i)$ are the spherical coordinates of the ith ion of crystal lattice in the system of reference centered at the impurity ion. Averaged value $\langle r^4\rangle = 1.52858$ a.u.^{4} of 4th power of the r radial coordinate of the d electrons of impurity ion, was calculated using the wave functions from [21,22], and the expressions for the polynomials V_4^0 are given in [20]. Overlap integrals between *d*-functions of the central ion and *p*- and *s*-functions of the ligands, denoted by $S_s = \langle d0|s0\rangle$, $S_\sigma = \langle d0|p0\rangle$, $S_\pi = \langle d1|p1\rangle$, were calculated numerically using, also, the wave functions from [21,22]. They were approximated by the following functions of distance R ($2.9 < R < 4.0$, atomic units) [23]:

$$\begin{aligned} S_s &= \langle d0|s0\rangle = -0.3229 + 0.063363R \\ S_\sigma &= \langle d0|s0\rangle = 0.27169 - 0.054574R \\ S_\pi &= \langle d1|p1\rangle = 1.4757\exp(-0.94354R) \end{aligned} \tag{4}$$

G is dimensionless adjustable parameter of the model, which was determined from the positions of the first absorption band of the system. Knowledge dependence of $10Dq$ parameter on interionic distance R between Mn^{2+} impurity ion and O^{2-} ligands of $[MnO_6]^{10-}$ cluster, does not only play a key role in the impurity ion energy levels splitting, but can help to estimate the EVI constants, HR parameters and E_{JT} [17].

A semi-empirical analysis of $10Dq$ dependence on R distance for Mn^{2+}–O^{2-} ions in doped MgO:Mn^{2+}, in the framework of ECM [20] is presented in this paper. This dependence was used for estimation of EVI constants in first approximation, HR factors and E_{JT} in the $^4T_{2g}$ excited state of manganese ion coupled with the a_{1g} and e_g normal modes of MgO host matrix.

Ham quenching of spin–orbit splitting of $^4T_{2g}$ energy level, described by the effective second-order spin-Hamiltonian, is also analyzed. The HR parameters and E_{JT} were estimated through Ham reduction parameter, γ, using the effective e_g frequency calculated in the Section 4. The obtained results, by two methods, are discussed, compared between them and with experimental data.

The structure of the paper is as follows: in the next section we briefly describe the crystal structure of the considered system, then presented the obtained results and conclude the paper with a brief summary.

2. Geometry optimization

MgO is a cubic crystal belonging to the space group No. 225 in International Table of Crystallography, with the lattice constant $a = 4.211$ Å and equilibrium distance Mg^{2+}–O^{2-} equal to 2.1055 Å [24]. Unit cell of MgO contains 8 ions: $4Mg^{2+}$ and $4O^{2-}$ in (4a) and (4b) Wyckoff positions respectively. Each Mg^{2+} ion is surrounded by six oxygens in an perfect octahedral symmetry. Full optimization of the a lattice parameter as well as the (x,y,z) internal coordinates of the ions, needed for reliable calculation with Eqs. (2) and (3), has been carried out.

The calculations were made with the CRYSTAL09 computer program [25,26] within the framework of density functional theory (DFT), with the hybrid functional B3LYP. The B3LYP is Becke's three-parameters functional [27] combined with the non-local correlation functional LYP [28] and in addition Hartree–Fock exchange. It is widely and successfully used in molecular quantum chemistry as well as in solid state calculations, where it has been shown to reproduce equilibrium geometries and vibrational frequencies in good agreement with experiment [29]. Mg^{2+}, Mn^{2+} and O^{2-} ions centers are described with basis sets taken from the Crystal 09 web site [30].

Diagonalization of the Fock matrix was performed at adequate k-point grids in the reciprocal space which is the Pack–Monkhorst/Gilat shrinking factor IS = ISP = 4. The thresholds controlling the accuracy calculation of Coulomb and exchange integrals were set to 10^{-8} (ITOL1 to ITOL4) and 10^{-14} (ITOL5) which assures a convergence in total energy better than 10^{-11} a.u., whereas the percentage of Fock/Kohn–Sham matrix mixing was set to 40 (IPMIX = 40) [26].

By doping, the Mn^{2+} will substitute isovalent the Mg^{2+} in O_h site symmetry, which leading to an impurity-ligand equilibrium distance R_0 different from d. The new equilibrium distance Mn^{2+}–O^{2-}, $R_0 = 2.0073$ Å, has been calculated through the geometry optimization of the MgO:Mn^{2+} system, using $3 \times 3 \times 3$ supercell, with 216 atoms, with CRYSTAL 09 package [26].

In Fig. 1 is given the unit cell of MgO:Mn^{2+}, with four formula units, drawing in Vesta [31], with Mn^{2+} ions as green sphere, Mg^{2+} by blue spheres and O^{2-} ions as red spheres.

3. Computational details

$10Dq$(PC) and $10Dq$(EC) given by Eqs. (2) and (3) were calculated in ECM [20], based on optimized geometry of MgO:Mn^{2+} system. The $G = 1.78$ dimensionless adjustable parameter of the model, which enters in overlap integrals , was determined from the positions of the first absorption band, at 750 cm^{-1} [32,33].

For the equilibrium distance $R_0 = 2.0073$ Å we obtained $10Dq(\mathrm{PC}) = 3896.5$ cm^{-1}, $10Dq(\mathrm{EC}) = 3603.5$ cm^{-1} and $10Dq = 7500$ cm^{-1}. Based on the Eqs. (2) and (3), the numerical values of $10Dq$ for impurity-ligands distances, very close to equilibrium distance R_0, in steps of 1% with $R_0 \pm 5\%$, is reached. The results of calculation are collected in Table 1.

A graphical representation of $10Dq(R)$ dependence (PC, EC and the total contribution) for values of R near by the equilibrium distance is given in Fig. 2. As can see the approximating functions fit very well the calculated values.

4. Analysis of microscopic crystal field effects

If $10Dq$ dependence is written as $10Dq = \frac{K}{R^n}$ with $K = 419{,}828$ and $n = 5.785$, then the constants of EVI between $^4T_{2g}$ excited state

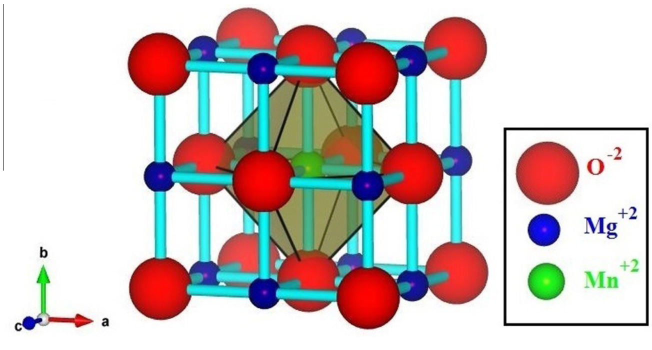

Fig. 1. Unit Cell of MgO:Mn^{2+} with four formula units.